Step bunching induced by flow in solution

doi: 10.1016/j.jcrysgro.2010.10.074

Step Bunching Induced by Flow in Solution

Masahide Sato

Information Media Center, Kanazawa University,

Kakuma-cho, Kanazawa 920-1192, Japan

(Dated: December 2, 2010)

Abstract

By carrying out Monte Carlo simulations, we study step bunching induced by flow in solution during dissolving. For simplicity, we assume that steps are straight and express an array of steps as dots on one-dimensional vicinal face. We consider a two square lattice to represent the diffusion field in a solution. The diffusion of atoms in a solution is expressed as the hopping of atoms on lattice sites. During dissolving, the step bunching occurs in the case of step-up flow. In an early stage, the width of the fluctuation of step distance, w, increases with time as t^{α}. The exponent α is equal to $1/2$ in the initial stage. Then, α decreases and is approximately given by $1/4$. In a late stage, the width w is saturated. The saturated value of w increases with the strength of flow.

PACS numbers: 81.10.Aj, 05.70.Ln, 47.20.Hw, 68.35.Fx

Keywords: A1. Crystal morphology, A1. Growth Models, A1. Morphological instability, A1. Surfaces

I. INTRODUCTION

On the vicinal face, which consists of an equidistant array of straight steps, the steps show two types of instabilities. One is step bunching, which is the instability for fluctuation of step distance, and the other is step wandering, which is the instability for fluctuation along steps. These instabilities are often observed when a vicinal face grows from solution. The step wandering induced by the flow in a solution occurs on a growing vicinal face. From a linear stability analysis [1], Potapenko showed that step wandering is induced owing to the step-up flow. In an experiment [2], step wandering is observed on a growing KH_2PO_4 (KDP) crystal. The direction of the flow agrees with the theoretical prediction [1].

The step bunching is also caused by the flow in a solution. Chernov and coworkers [3–5] theoretical studied. In their model, the step density is so high that the vicinal face is treated as a linear sink of atoms. They assumed that kinetic coefficient is proportional to the step density. From the linear stability analyses and numerical studies [3–5], a growing vicinal face is unstable for a long-wavelength fluctuation owing to the step-down flow. Bredikhin and coworkers [6, 7] derived the nonlinear evolution equation of step density and studied the behavior of the unstable vicinal face. From numerical simulations of the nonlinear equation, a quasi-regular array of high step density appears. The form of the array is similar to that of bunches observed in the experiments [6–8].

In the previous studies [3–6], the step density is assumed to be so high that the vicinal face is treated as the line sink of atoms in a solution. The behavior of the step density has been investigated, but the motion of each step has not been sufficiently studied. Thus, in this paper, to study the motion of steps during the step bunching we consider a simple model in which a flow in a solution is taken into account, and carry out Monte Carlo simulation. We assume that the steps are straight and treat the steps as points on a one-dimensional vicinal face. To represent the diffusion filed in a solution, we consider a two-dimensional lattice. In our previous study [9], we studied the bunching in a growing vicinal face. In this paper, we study how the steps behave during the step bunching on a melting vicinal face.

In Sec.II, we introduce our simplified model. In Sec. III, we carry out Monte Carlo simulations and investigate how the motion of steps changed owing to the flow. We study the growth law of the width of fluctuation of step distance. We summarize the results in Sec. IV.

II. MODEL

To carry out Mote Carlo simulation, we use a very simplified model (Figure 1). We mainly simplify the form of steps, the diffusion of atoms in solution and the flow in solution.

We assume that steps are straight and consider a one-dimensional vicinal face. The x-direction is the step-down direction. We neglect the height of steps and treat a vicinal face as a line. Thus, the steps are treated as points on the line. The steps advance to x-direction on a line during growth. The vicinal face is placed at $z = 0$, and the altitude in solution is measured from the vicinal face.

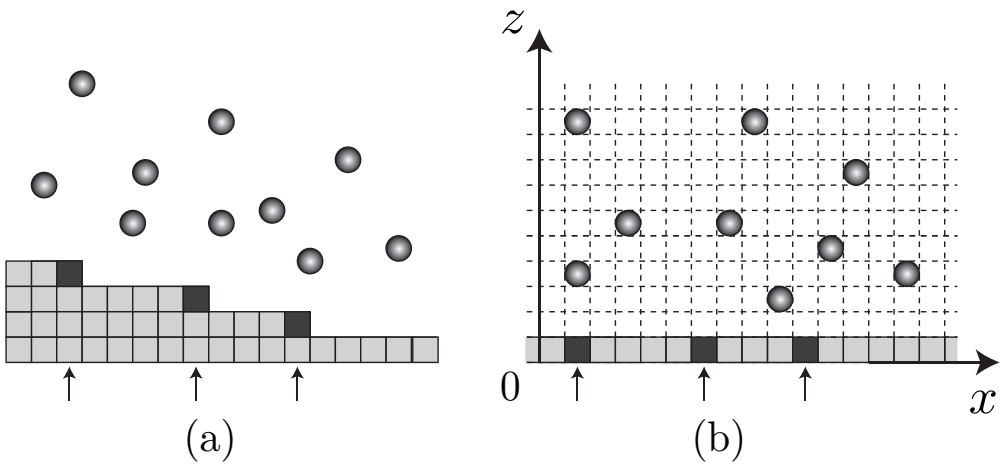

FIG. 1: Schematic figures of (a) a vicinal face and (b) our model, respectively. Circles are atoms in a solution and squares are solid atoms. Dark squares represent the solid atoms at step edge. Arrows show the positions of steps.

In our simulation, active atoms are atoms at step edges and atoms in a solution. In each Monte Carlo trial, we randomly choose one active atom. If the chosen atom is an atom in a solution, we carry out a diffusion trial. The flow in a solution is expressed as bias in the diffusion probability [10, 11]. When an atom at the site (i, j) is chosen, the atom moves to the sites $(i, j \pm 1)$ with the probability $1/4$ and to the sites $(i \pm 1, j)$ with the probabilities $p_{\pm} = (1 \pm p_{\rm flow})/4$, where $p_{\rm flow}$ represents the flow rate in a solution. Owing to the viscosity in solution, the flow should be weak near the vicinal face and vanish on a vicinal face. Thus, for simplicity, we assume that $p_{\rm flow} = p^0_{\rm flow}(j - 1)$. The sign of $p^0_{\rm flow}$ shows the direction of the flow: the flow is in the step-down direction with a positive $p^0_{\rm flow}$ and in the step-up direction with a negative $p^0_{\rm flow}$. If the altitude is so high that $p_{\rm flow} > 1$ or $p_{\rm flow} < -1$, we

set the hopping probabilities p_+ and p_- to be 1 and 0 or 0 and 1, respectively. For the diffusion coefficient D to be 1, the increment of the time in each diffusion trial is given by $\Delta t = 1/4N_{\rm s}$, where $N_{\rm s}$ is the number of atoms in a solution. When an atom in a solution

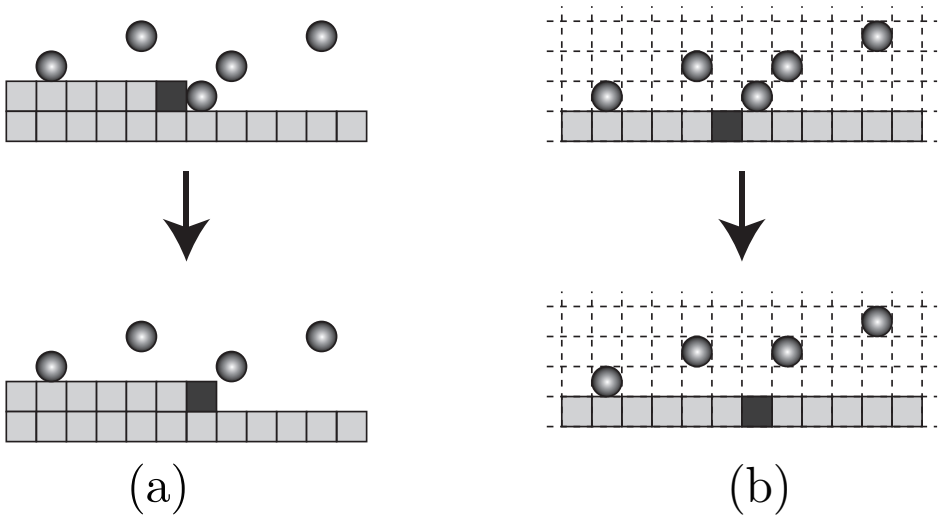

FIG. 2: Schematic figure of solidification process in (a) the vicinal face and (b) our model. Circles and squares represent atoms in a solution and solid atoms, respectively. Dark square represents an atom at a step edge.

arrives at the vicinal face after diffusion trials, solidification occurs with the probability [12]

$$p_{\rm s} = \frac{1}{e^{-\phi/k_{\rm B}T}+1}, \tag{1}$$

where ϕ is the chemical potential gain by solidification of an atom. When the position of an atom is $(x_{\rm atom}, 1)$ and a step is present at $x_{\rm atom}-1$, the step advances to $x = i_{\rm atom}$ and the atom in the solution vanishes after solidification (Figure 2).

When an atom at a step edge is chosen, melting occurs with the probability [12]

$$p_{\rm m} = \frac{1}{e^{\phi/k_{\rm B}T}+1}. \tag{2}$$

If the position of the melted atom is $x_{\rm step}$, the step edge recedes to $x_{\rm step}-1$ and an atom is expelled to the site $(x_{\rm step}, 1)$ (Figure 3). If the site $(x_{\rm step}, 1)$ is already occupied by another atom, melting is not tried.

We assume that kinetics coefficient of steps is so large that the density of atoms is in equilibrium at step edges. Thus, the detail balance stands up at step positions. The

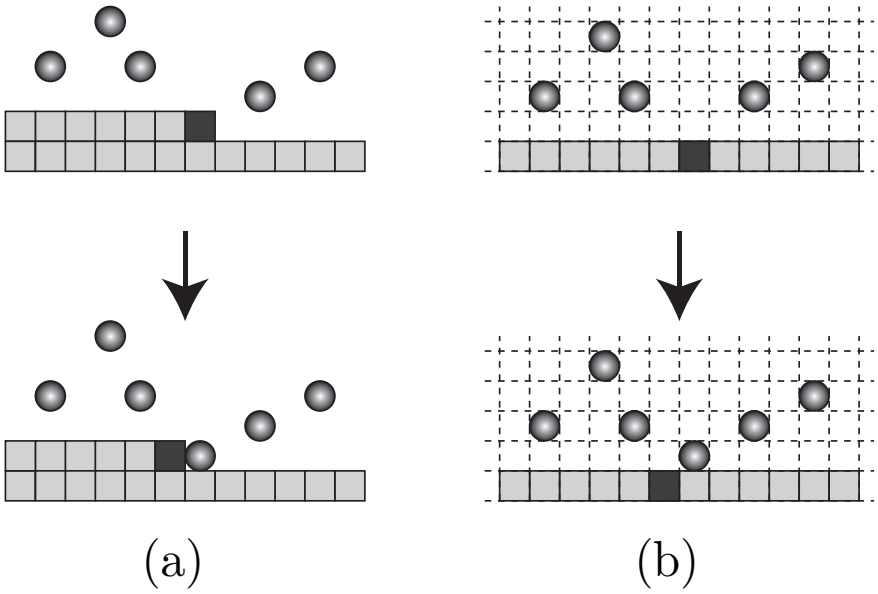

FIG. 3: Schematic figure of melting process in (a) a vicinal face and (b) in our model. Circles and squares represent atoms in a solution and solid atoms, respectively. Dark square represents an atom consisting steps.

equilibrium concentration in a solution, $c_{\rm eq}$ satisfies the relation, $c_{\rm eq}p_{\rm s} = (1 - c_{\rm eq})p_{\rm m}$. The equilibrium adatom density is expressed as [12]

$$c_{\rm eq} = \frac{1}{e^{\phi/k_{\rm B}T} + 1}. \tag{3}$$

In our model, when the altitude is larger than the critical value $z_{\rm max}$, the concentration of atoms becomes constant value $c_{\rm max}$. If the density of atoms $c_{\rm max}$ is lower than $c^0_{\rm eq}$, melting occurs more frequently than solidification and the steps recede.

III. RESULTS OF SIMULATION

In the previous study [9], we studied the time evolution of step positions during growth. Hereafter, we focus on the time evolution during dissolving. Figure 4 shows typical time evolutions of step positions. The system sizes in the x-direction and z-direction are $L_x = 512$ and $L_z = 128$. The number of steps is 16. The critical altitude $z_{\rm max}$ is 96, and the density of atoms in $z > z_{\rm max}$ is $c_{\rm max} = 0.0$. Since the chemical potential gain ϕ is equal to 2.0, the equilibrium density of atoms is given by $c_{\rm eq} = 0.12$. Thus, melting occurs more frequently than solidification and steps recede.

Figure 4 shows the time evolution of step positions. The formation of step bunches depends on the direction of flow in a solution. When the flow is in the step-up direction (Fig. 4(c)), an equidistant train of steps is unstable and step bunching occurs. Small bunches are produced in the initial stage. The bunch size grows by coalescence of small bunches. When the flow is in the step-down direction (Fig. 4(b)) and absent (Fig. 4(a)), small bunches seem to be formed by fluctuation in the initial stage, but the bunches do not grow and large bunches are not produced in a late stage. The dependence of formation of bunches on the flow agrees with the stability analysis [3].

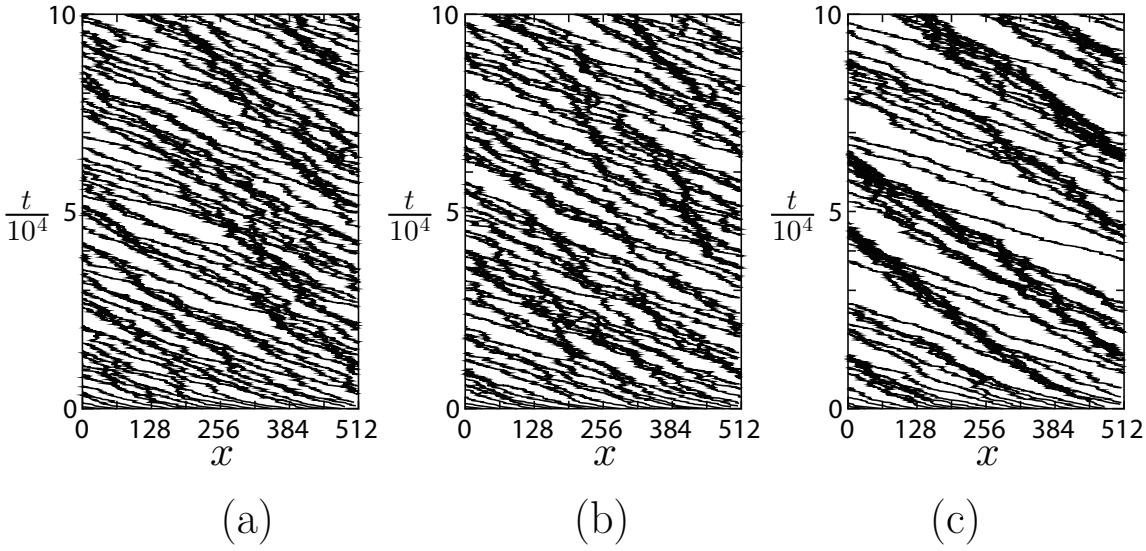

FIG. 4: Time evolution of step positions with (a) $p^0_{\rm flow} = 0.0$, (b) $p^0_{\rm flow} = 0.01$. and (c) $p^0_{\rm flow} = -0.01$.

Figure 5 shows the time evolutions with various negative $p_{\rm flow}$. With increasing $|p_{\rm flow}|$, bunches grow faster and become tighter. The dependence of the velocity of bunch on the bunch size is obviously seen in the initial stage of Fig. 5(a), The velocity of bunch decreases with increasing the bunch size. Once a bunch which is slightly larger than the other is formed, smaller bunches collide with the bunch from the lower side and bunch size increases. We also see the collision caused by the difference of the bunch velocity owing to the difference of bunch size at $t \sim 5 \times 10^4$ in Fig. 5(b). Since a small bunch recedes faster, the collision of two bunches occurs at $x \approx 380$.

Figure 6 shows the time evolution of the width of the fluctuation of step distance w,

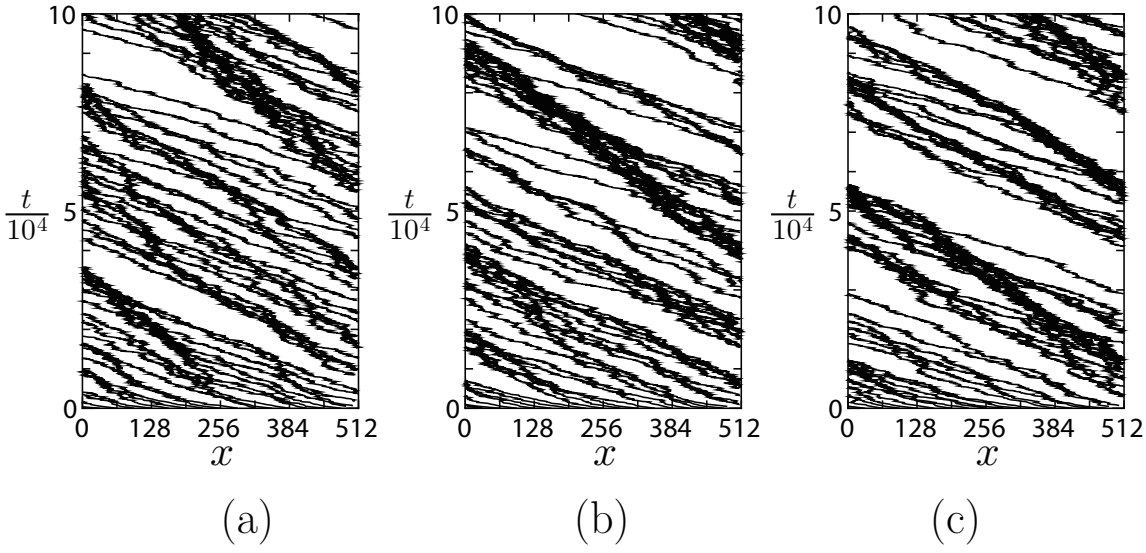

FIG. 5: Time evolution of step positions with (a) $p^0_{\rm flow} = -0.005$, (b) $p^0_{\rm flow} = -0.05$, and (c) $p^0_{\rm flow} = -0.1$. The other parameters are the same as those in Fig. 4.

which is defined as

$$w = \sum_{j=1}^{N} \sqrt{\frac{1}{n_{\rm s}} \sum_{i=1}^{n_s} [l_j(i) - \bar{l}]^2}. \tag{4}$$

N is the number of samples, $n_{\rm s}$ is the number of steps, $l_j(i)$ is the width of ith terrace in the jth sample, and $\bar{l}$ is the average terrace width. Both with step-down flow and without flow, the width w increases with time owing to thermal fluctuation, but large bunches are not formed. The width w is saturated in an early stage with a small value. The saturated value of w with step-down flow is as large as that without the flow, but saturation of w with step-down flow occurs slightly faster than that without flow. When the flow is in the step-up direction, w increases in an early initial stage owing to step bunching. The width w during $t \leq 3 \times 10^3$ grows faster than that during $3 \times 10^3 \leq t \leq 6 \times 10^4$. In a late stage, the width is saturated. The saturated value of the width is much larger than that without the flow.

Figure 7 shows the early stage of the time evolution of w with step-up flows. In an early stage, the width w increases as t^α. The value of α changes with time. Initially, α is equal to 1/2. Then, α decreases and is given by 1/4. With increasing the flow rate, the growth with $\alpha = 1/2$ ends early and the time interval with $\alpha = 1/4$ becomes longer. Figure 8 shows the time evolution of step positions in the late stage. Owing to gathering of small bunches, a large bunches is temporarily formed. However, the bunch is unstable and broken

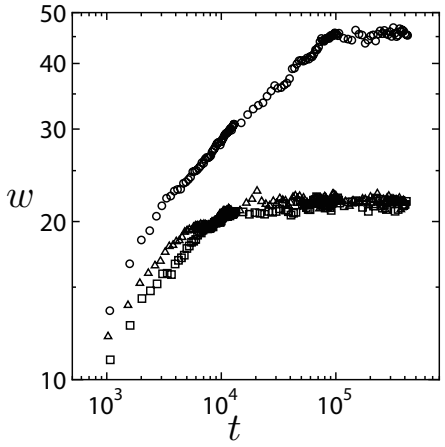

FIG. 6: Time evolution of the width of fluctuation of step distance with $p^0_{\rm flow} = -0.1$ (◯), $p^0_{\rm flow} = 0$ (△), and $p^0_{\rm flow} = 0.1$ (□).

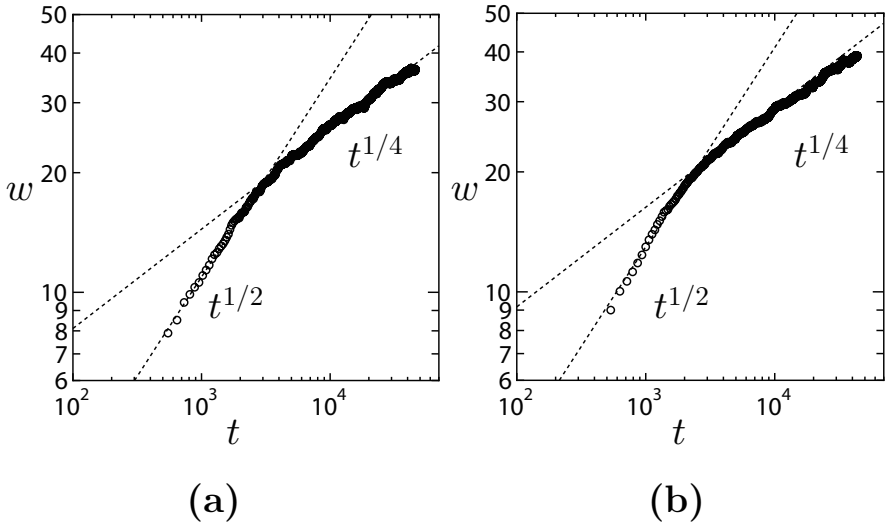

FIG. 7: The initial stage of the time evolution of w (a) with $p^0_{\rm flow} = -0.01$, (b) with $p^0_{\rm flow} = -0.1$. The other parameters are the same as those in Fig. 4.

into small bunches again. The repeat of formation of large bunches and break of them causes the saturation of the width w. Figure 9 shows the dependence of saturated value of the width, $w_{\rm s}$ on $p_{\rm flow}$. When the flow rate is slow, the saturated width $w_{\rm s}$ increases with increasing velocity of the flow $p_{\rm flow}$. When the flow rate $p^0_{\rm flow}$ is small, the width $w_{\rm s}$ increases as $w_{\rm s} = p^{3/20}_{\rm flow}$. When $p_{\rm flow}$ is sufficiently large, $w_{\rm s}$ appears to be saturated. The behavior is similar to that during growth [9].

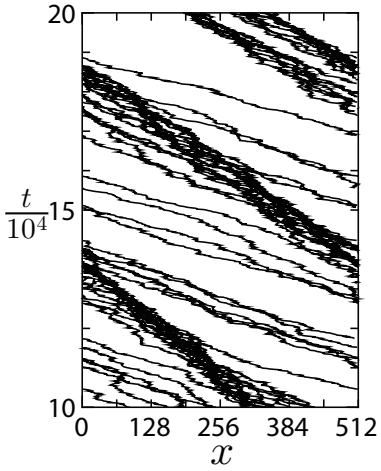

FIG. 8: The late stage of the time evolution of step positions with $p^0_{\rm flow} = -0.1$. The other parameters are the same as those in Fig. 4.

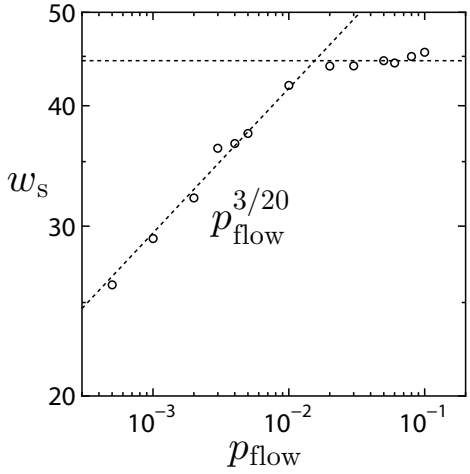

FIG. 9: Dependence of the saturated value of w. Except for the flow rate $p^0_{\rm flow}$, parameters are same as those in Fig. 4.

IV. SUMMARY

In this paper, to study step bunching induced by flow in a solution during dissolving, we introduced a very simplified model and carried out Monte Carlo simulations. When the flow in a solution is in the step-up direction, a vicinal face is unstable and step bunching occurs. The direction to cause the step bunching agrees with a linear stability analysis [3].

In early stage, bunches grow owing to coalescence of small bunches. With increasing the flow rate $p^0_{\rm flow}$, the bunches become tighter and grow faster. the width of the fluctuation of

step distance, w increases with time as t^{α}. Initially, the exponent α is equal to 1/2. Then, α decreases and becomes 1/4. In the time interval with $\alpha = 1/2$, small bunches are formed by the pairing of steps and coalescence of step pairs. The break of bunches hardly occurs. In the time interval with $\alpha = 1/4$, though the frequency of breaking of bunches is low, both the coalescence of bunches and the break of bunches occur. The difference in the step behavior probably causes the difference in the exponent α. In our previous study [9], we reported that $\alpha = 1/3$ during growth [9]. The value of α during growth appear to be different from that during melting. However, the fluctuation of data is large and the time evolution is determined form a few points of data. Thus, we intend to investigate the exponent during growth in detail. In a later stage, the coalescence and breaking of bunches repeatedly occurs, which causes the saturation of the size of bunch. For small $p_{\rm flow}$, the saturated width $w_{\rm s}$ increases as $p_{\rm flow}^{\beta}$ with $\beta = 3/20$, and $w_{\rm s}$ is saturated with large $p_{\rm flow}$. Thus, the direction of the motion of steps is opposite, the behavior of bunches during melting is similar to that during growth.

In previously, Kwon and a coworker [13] studied the motion of a vicinal face with taking account of both the surface diffusion field and the bulk diffusion. They numerically solved the diffusion equations and determined step velocities. In their study [13], they investigated the time evolution of terrace widths during surface diffusion growth, but they did not show the motion of steps during the bulk diffusion growth. By using their model, we probably find the effect of the bulk diffusion filed, which is not rigorously taken into account in our simplified model. In previous studies [6, 7], the step bunching occurs without flow. In their model, however, effect of the velocity of the step motion to the diffusion equation is taken into account. The motion of steps acts as relative flow for solution. If the steps recede faster in our model, the step bunching probably occurs without flow.

For simplicity, we assumed that the steps are straight. Thus, step wandering, which is the instability for the fluctuation along steps, can not be treated in our model. To study the step wandering, we are now going to carry out simulation with the two-dimensional step model.

Acknowledgments

This work is supported by Grants-in-Aid for Scientific Research from Japan Society for the Promotion of Science.

---

[1] S. Y. Potapenko: J. Cryst. Growth **158** (1996) 346.

[2] H. F. Robey, S. Y. Potapenko: J. Cryst. Growth: **213** (2000) 355.

[3] A. A. Chernov: J. Cryst. Growth **118** (1992) 333.

[4] A. A. Chernov, S. R. Coriell and B.T. Murray, Journal of Crystal Growth, **132** (1993) 405.

[5] S. R. Coriell, B. T. Murray, A. A. Chernov, G. B. McFadden, Journal of Crystal Growth, **169** (1996) 773.

[6] V.I. Bredikhin and O.A. Malshakova, Journal of Crystal Growth, **303** (2007) 74.

[7] V.I. Bredikhin, O.A. Malshakova and A. D. Yunakovsky, Journal of Crystal Growth, **312** (2010) 1443.

[8] V.I. Bredikhin, G. L. Galushkina, A. A. Kulagin, S. P. Kuznetsov, O. A. Malshakova, Journal of Crystal Growth, **219** (2000) 83.

[9] M. Sato, Journal of Phys. Soc. Jpn., **79** (2010) 064606.

[10] M. Sato, M. Uwaha and Y. Saito, Phys. Rev. Lett., **80** (1998) 4233.

[11] M. Sato, M. Uwaha and Y. Saito, Phys. Rev. B **62** (2000) 8452.

[12] Y. Saito and M. Uwaha, Phys. Rev. B, **49** (1994) 10677.

[13] Yong-ll Kwon, Jeffery J. Derby, Journal of Crystal Gowth, **230** (2001) 328.